

Appln. No. 10/524,039
Appeal Brief

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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
STEPHAN BAUER, ET AL : GROUP: 1796
SERIAL NO: 10/524,039 :
FILED: FEBRUARY 9, 2005 : EXAMINER: COONEY, J.
FOR: METHOD FOR THE PRODUCTION :
OF LOW-EMISSION
POLYURETHANE SOFT FOAMS

APPEAL BRIEF

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

The following is an appeal to the Board of Appeals concerning the decision by the Examiner to finally reject pending Claims 17-20 and 22-32 of the above-identified application as follows:

REAL PARTY OF INTEREST

BASF SE is the real party of interest in the above-identified application.

RELATED APPEALS AND INTERFERENCES

There are no applications on appeal or in interference that are related to the present application.

STATUS OF CLAIMS

Claims 1-16 and 21 have been canceled. Claims 17-20 and 22-32 are pending and on appeal.

STATUS OF AMENDMENTS

No amendment to the Office Action of November 10, 2008 has been filed.

SUMMARY OF CLAIMED SUBJECT MATTER

The present invention is directed to a low-emission producing, flexible polyurethane foam by reacting a) a polyisocyanate with b) a compound having at least two hydrogen atoms which are reactive toward an isocyanate group, wherein the compound is a polyether alcohol which has been prepared by addition of an alkylene oxide to a compound derived from renewable raw materials selected from the group consisting of castor oil, polyhydroxy fatty acids, ricinoleic acid, hydroxyl-modified oils, grapeseed oil, black caraway oil, pumpkin seed oil, borage seed oil, soybean oil, wheat germ oil, rapeseed oil, sunflower oil, peanut oil, apricot kernel oil, pistachio nut oil, almond oil, olive oil, macadamia nut oil, avocado oil, sea buckthorn oil, sesame oil, hemp oil, hazelnut oil, evening primrose oil, wild rose oil, hemp oil, safflower oil, walnut oil, hydroxyl –modified fatty acids and fatty acid esters myristoleic acid, palmitoleic acid, oleic acid, vaccenic acid, petroselinic acid, gadoleic acid, erucic acid, nervonic acid, linoleic acid, α - and γ -linolenic acid, stearidonic acid, arachidonic acid, timnodonic acid, clupanodonic acid, cervonic acid in the presence of a DMC catalyst, said polyether alcohol having a maximum odor value of 2.0 or less. The flexible polyurethane foam product has a maximum VOC value of 100 ppm and a maximum FOG value of 200 ppm, according to the methods of determining VOC and FOG values as described in “Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption” (PB VWL 709), DaimlerChrysler, January 2001.

Support for the scope of the process as claimed can be found on page 3, lines 25 to 40; page 4, lines 11 to 30 and page 5, lines 27 to 40 of the text of the specification.

GROUND OF REJECTION TO BE REVIEWED

Whether Claims 17-20 and 22-32 stand properly rejected based on the first paragraph of 35 USC 112.

Whether Claims 17-20 and 22-32 stand properly rejected based on 35 USC 103 as unpatentable over Sugiyama et al, U. S. Patent 6,313,060 in view of JP-05163342.

ARGUMENT

Claim Rejection, 35 USC 112

Appellants do not agree that the written description is defective in that it fails to convey to one of skill in the art that the inventors, at the time the application was filed, had possession of the claimed invention. The specification of the present application on page 2 provides a sufficient discussion of the problem of emissions of condensable materials from flexible polyurethane foams and describes a system of determining the extent of emissions in terms of FOG and VOC values. The actual maximum FOG and VOC values of the present claims are described in the last paragraph of page 3 of the specification. During prosecution in order to make clear how the FOG and VOC values were and are determined, an English translation of the flexibility after aging test mentioned on page 3, lines 11-16 of the specification was submitted along with a printed document describing the well known test procedures for determining the VOC and FOG values identified as PB VWL 709 (see page 4, lines 11-30 of the specification).

The Examiner has objected to the so-called foreign test standard that is present in the claims which describes the specific steps which are followed in order to determine VOC and

FOG values of flexible polyurethane foams of the invention, simply because the standard procedure referred to is said to be of foreign origin and therefore non-enabling of the present invention. This is manifestly incorrect. In the first place the document is written in English, not German (although a German language document of the specifications exists.). Specific steps are described as to how to determine VOC and FOG values so that the document provides at the very least a precise description of the methodology to be followed in order to determine these values. The steps of analysis to be followed leave nothing to guess-work. In fact, as stated on page 2, lines 30-34, the test method PB VWL 709 is an established commercial test method that has gained wide acceptance within the automobile industry.

Further, the document can not be said to be “foreign” because, at the very least, the Chrysler component of DaimlerChrysler is a former major U. S. automaker. Obviously, therefore, the procedures described in the document in question were known at the very least to workers of Chrysler in the American automobile industry. However, quite likely the disclosure of the standard test is well known to other automobile manufacturers in the U. S. beyond DaimlerChrysler. Further, there is nothing indefinite about the written standard so that one of skill in the art would be enabled by the disclosure of the document to obtain needed VOC and FOG values for a flexible polyurethane foam. Appellants therefore believe that the non-reference ground of rejection has been rendered null and void.

Claim Rejection, 35 USC 103

As is clear from the present specification at page 2, attempts have been made to produce flexible polyurethane foams from polyether alcohols that have been prepared from what is termed renewable raw materials such as castor oil. Basic catalysts such as sodium and potassium hydroxides and alkoxides have been used to facilitate the polyether alcohol forming reaction, but upon the formation of a foamed polyurethane product, the product exhibits very poor odor, fogging and emissions properties. For instance, when castor oil is

employed as the initiator, considerable amounts of ricinoleic acid are formed. This ring containing material can only be removed incompletely by simple steam stripping. The polyether alcohol product and foams produced therefrom display unacceptable odor, fogging and emissions characteristics. The foams produced therefore are not commercially acceptable products. With regard to castor oil specifically, as a renewable raw material, the result is a foamed polyurethane product that contains substantial amounts of cyclic fatty esters which exhibit unacceptably high levels of emissions as is evident from the VOC and FOG values normally obtained.

Directing attention now refer to the cited JP '342 reference, here the inventors addressed the problem accompanying the use of castor oil as an initiator for the preparation of polyether alcohols in which the use of an alkali catalyst known conventionally for this reaction resulted in the decomposition of the double bond in the material. On the other hand, when a Lewis acid catalyst is used for the reaction, the problem encountered there was that the amount of polyether prepared was unsatisfactory. These problems with respect to polyether alcohol synthesis are solved in '342 for the specific reaction of castor oil and alkylene oxide by the use of a metallocyanide complex compound as the catalyst. It is to this problem that essentially all of the disclosure of '342 is directed. Only the briefest mention (general in nature) of the use of the specific polyether alcohol of the reference as the polyol for the preparation of a polyurethane upon reaction with an isocyanate is provided at paragraph [0027]. Nothing is said in the reference about the problems of odor, FOG and VOC mentioned in the present invention. Nothing is said about the preparation of polyurethane foams. There is not the slightest teaching or suggestion that would lead one of skill in the art to expect that if a polyether alcohol, prepared by metallocyanide complex catalyzed reaction of castor oil with an alkylene oxide, is used in a reaction with a polyisocyanate to prepare a

foamed polyurethane product, that the product obtained would exhibit satisfactory emissions characteristics as evidenced by reduced odor and low VOC and FOG values.

The disclosure of the cited Sugiyama et al patent is directed to a method of preparing a resilient polyurethane foam material by reacting a polyisocyanate with a polyether alcohol that is prepared by the ring opening reaction of an alkylene oxide compound that has carbon atom content of at least 3 with an initiator which is a monohydroxy initiator such as methanol, isopropyl alcohol, butanol or the like (col 8, lines 5-10), or a polyhydroxy compound containing 2 to eight hydroxyl groups such as sorbitol, sucrose, pentaerythritol, or the like (col 8, lines 15-20) in the presence of a double metal cyanide complex catalyst. The objective sought in the patent is to prepare such a foamed material that has much improved crushing and cushioning properties over those known to the prior art. For the preparation of the polyether alcohol reactant, no initiator that is a renewable raw material detailed as in the present claims is shown or suggested. Not only that, there is no description of the problem faced in the particular area of preparing foamed polyurethanes from polyether alcohols in turn prepared from initiators of renewable raw materials, nor is there any suggestion that the problem elucidated on the record of VOC, FOG and odors emanating from conventional polyurethane foams in turn prepared from polyether alcohols obtained from renewable raw materials can be eliminated.

Another aspect of the disclosure of the '060 patent which mitigates against its combination with '342 is that the procedure of preparing a polyether polyol is more complex than either that of the present claims or the procedure of '342. That is, the patent deems it necessary in the preparation of a polyether alcohol, that if a metallocyanide complex is to be used as a catalyst for the preparation of the polyether alcohol, the initiator must be reacted with an alkylene oxide having a carbon atom content of at least 3 (see col 3, lines 46-52 or col 8, lines 5-20). By this definition, specifically, ethylene oxide is excluded as a reactant. If,

however, ethylene oxide is to be employed also in the polyether forming reaction, **it must be done so using a conventional alkali metal hydroxide or alkoxide catalyst**. (See col 7, lines 49-55 and col 8, lines 5-20). No such conditions are imposed upon the polyether alcohol forming reaction of the present claims!

The Examiner stated in the bottom paragraph of page 3 of the final Office Action that Sugiyama et al *is not limited only to the specific initiator exemplified*. To the contrary, appellants submit that the disclosure of the patent is limited to an initiator that is a monol or is a polyol compound that expressly contains from 2 to 8 hydroxy groups. Thus, compounds such as various glycols, glycerol and other trihydroxy compounds, as well as a sugar, a sugar alcohol and alcohol amines. Nowhere in this group of varieties of polyols is mention made of a renewable raw material as claimed in the present invention.

The Examiner also states (on page 3 of the Office Action) that the '3342 reference discloses the preparation of *polyols made from initiators as defined by applicants' claims*. This is not correct. The reference discloses a polyol made by the reaction of castor or denatured castor oil only as an initiator with an alkylene oxide. No other renewable raw material is disclosed, and certainly no examples of foamed polyurethanes are disclosed. The combined references simply do not compel or motivate the skilled artisan to make an advance in the technology of foamed polyurethane materials as to their important emission characteristics by employing a different catalyst system for preparation of the foamed material. Yet the maximum VOC and FOG values are positively claimed in the present claims where a foamed product of improved emission characteristics is obtained.

Claims 17-20

Each of these claims is directed to a specific product, each being dependent upon the foamed polyurethane product produced by the process of Claim 22. None of these products is shown or suggested in the cited and applied prior art, neither of which teaches or suggests a

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foamed flexible polyurethane prepared by the DMC catalyzed reaction of a polyisocyanate with a polyether alcohol which in turn is obtained from a reaction involving a renewable raw material. Accordingly, each of these products is believed separately patentable.


Appellants maintain that the continued rejection of the present claims is erroneous and that the decision by the Examiner should be REVERSED.

Respectfully submitted,

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CLAIM APPENDIX

The following is a list of pending claims in the application.

Claim 17. A low-emission flexible polyurethane slabstock foam produced by the process as claimed in claim 22.

Claim 18. A motor vehicle comprising said low-emission flexible polyurethane slabstock foam as claimed in claim 17.

Claim 19. An article of furniture or a mattress comprising said low-emission flexible polyurethane slabstock foam as claimed in claim 17.

Claim 20. The low-emission flexible polyurethane slabstock foam as claimed in claim 17 having reduced crack formation.

Claim 22. A process for producing low-emission flexible polyurethane foams by reacting:

- a) a polyisocyanate with
- b) a compound having at least two hydrogen atoms which are reactive toward an isocyanate group,

wherein said compound is a polyether alcohol which has been prepared by addition of an alkylene oxide to a compound derived from renewable raw materials selected from the group consisting of castor oil, polyhydroxy fatty acids, ricinoleic acid, hydroxyl-modified oils, grapeseed oil, black caraway oil, pumpkin seed oil, borage seed oil, soybean oil, wheat germ oil, rapeseed oil, sunflower oil, peanut oil, apricot kernel oil, pistachio nut oil, almond oil, olive oil, macadamia nut oil, avocado oil, sea buckthorn oil, sesame oil, hemp oil,

hazelnut oil, evening primrose oil, wild rose oil, hemp oil, safflower oil, walnut oil, hydroxyl-modified fatty acids and fatty acid esters myristoleic acid, palmitoleic acid, oleic acid, vaccenic acid, petroselinic acid, gadoleic acid, erucic acid, nervonic acid, linoleic acid, α - and γ -linolenic acid, stearidonic acid, arachidonic acid, timnodonic acid, clupanodonic acid, cervonic acid in the presence of a DMC catalyst, said polyether alcohol having a maximum odor value of 2.0 or less; and wherein the flexible polyurethane foam product has a maximum VOC value of 100 ppm and a maximum FOG value of 200 ppm, according to the methods of determining VOC and FOG values as described in "analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption" (PB VWL 709), DaimlerChrysler, January 2001.

Claim 23. The process as claimed in claim 22, wherein said polyether alcohol has a mean molecular weight M_w in the range from 400 to 10,000 g/mol.

Claim 24. The process as claimed in claim 22, wherein said polyether alcohol has a mean molecular weight M_w in the range from 1000 to 8000 g/mol.

Claim 25. The process as claimed in claim 22, wherein said polyether alcohol has a content of cyclic fatty acid esters of not more than 50 ppm.

Claim 26. The process as claimed in claim 22, wherein said polyether alcohol has a content of cyclic fatty acid esters of not more than 10 ppm.

Claim 27. The process as claimed in claim 22, wherein said low-emission flexible polyurethane foam has a wet compressive set of not more than 7 %, as determined in accordance with the operating procedure identified as AA U10-131-041 of February 6, 2002.

Claim 28. The process as claimed in claim 22, wherein said low-emission flexible polyurethane foam has a compressive set, after aging in accordance with DIN EN ISO 2440, of not more than 10 %.

Claim 29. The process as claimed in claim 22, wherein said polyisocyanate is an aliphatic diisocyanate, at least one aromatic diisocyanate or a polyisocyanate modified by incorporation of a urethane, uretdione, isocyanurate, allophanate, iretonimine or other group therein.

Claim 30. The process as claimed in claim 22, wherein said polyisocyanate is hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate, diphenylmethane diisocyanate or polymethylenepolyphenylene polyisocyanate.

Claim 31. The process as claimed in claim 22, wherein the polyether alcohol has an odor value of 1.7 or less, as determined by the standard test method identified as PPU 03/03-04.

Claim 32. The process as claimed in claim 22, wherein the flexible polyurethane foam product has a maximum VOC value of 50 ppm and a maximum FOG value of 100 ppm.

EVIDENCE APPENDIX

Appellants enclose copies of the European Standard Test EN ISO 2440 for determining the compressive set of flexible slabstock foams under accelerated aging conditions. Also enclosed is an English language copy of inhouse test procedures identified as PB VWL 709 for determining the VOC and FOG values of condensable substances discharged from vehicle interior materials by thermodesorption.

RELATED PROCEEDINGS APPENDIX

No copy of a decision rendered by a court or the Board in any proceeding identified pursuant to paragraph (c)(1)(ii) is enclosed.

English version

**Flexible and rigid cellular polymeric materials
Accelerated ageing tests
(ISO 2440 : 1997)**

Matériaux polymères alvéolaires
souples et rigides – Essais de
vieillissement accéléré
(ISO 2440 : 1997)

Weich- und Hartschaumstoffe –
Schnellalterungsprüfung
(ISO 2440 : 1997)

This European Standard was approved by CEN on 1998-06-21.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

The European Standards exist in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Foreword

International Standard

ISO 2440 : 1997 Flexible and rigid cellular polymeric materials – Accelerated ageing tests, which was prepared by ISO/TC 45 'Rubber and rubber products' of the International Organization for Standardization, has been adopted by Technical Committee CEN/TC 249 'Plastics', the Secretariat of which is held by IBN, as a European Standard.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, and conflicting national standards withdrawn, by May 2000 at the latest.

In accordance with the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard:

Austria, Belgium, the Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.

Endorsement notice

The text of the International Standard ISO 2440 : 1997 was approved by CEN as a European Standard without any modification.

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard specifies, for flexible and rigid cellular polymeric materials, laboratory procedures which are intended to imitate the effects of naturally occurring reactions such as oxidation or hydrolysis by humidity. The physical properties of interest are measured before and after the application of the specified treatments.

Test conditions are only given for open cellular latex, both open- and closed-cell polyurethane foams, and closed-cell polyolefin foams. Conditions for other materials will be added as required.

The effect of the ageing procedures on any of the physical properties of the material may be examined, but those normally tested are either the elongation and tensile properties, or the compression or indentation hardness properties.

These tests do not necessarily correlate either with service behaviour or with ageing by exposure to light.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 471:1995, *Rubber — Temperatures, humidities and times for conditioning and testing*.

3 Apparatus

3.1 For heat ageing

3.1.1 Oven, with forced circulation, capable of maintaining the required temperature to within ± 1 °C.

NOTE — It is recommended that a device be used to record the temperature, preferably continuously.

3.2 For humidity ageing

3.2.1 Ageing apparatus, of such a size that the total volume of the test pieces does not exceed 10 % of the free air space, and such that the test pieces are free of strain, freely exposed to the ageing atmosphere on all sides and not exposed to light.

3.2.2 Steam autoclave or similar vessel, capable of maintaining the required temperature to within ± 1 °C and of withstanding absolute pressures up to 300 kPa.

3.2.3 Glass vessel, with a suitable closure, and a **water-bath** or **drying oven** for heating the vessel, capable of maintaining the required temperature to within $\pm 1^\circ\text{C}$.

3.3 For physical-property measurements

Use apparatus appropriate to the measurements of the physical property to be examined.

4 Test pieces

4.1 Number, size and shape

The number of test pieces, and their size and shape, shall be appropriate to the property being examined. They shall be prepared, before ageing, to the dimensions used in the particular test.

4.2 Conditioning

Material shall not be tested less than 72 h after manufacture, unless at either 16 h or 48 h after manufacture it can be demonstrated that the mean result does not differ by more than $\pm 10\%$ from those obtained after 72 h. Testing is permitted at either 16 h or 48 h if, at the specified time, the above criterion has been satisfied.

Prior to the test, the test pieces shall be conditioned, undeflected and undistorted, for at least 16 h in one of the following atmospheres as given in ISO 471:

$23^\circ\text{C} \pm 2^\circ\text{C}$, $(50 \pm 5)\%$ relative humidity;

$27^\circ\text{C} \pm 2^\circ\text{C}$, $(65 \pm 5)\%$ relative humidity.

This period can form the latter part of the period following manufacture.

NOTE — It is recommended that for reference purposes the test be performed 7 days or more after the cellular material has been manufactured.

5 Procedure

5.1 General

After conditioning, the test of the required physical property shall be performed and the test pieces shall be brought rapidly to the ageing condition. If the test to be performed is destructive, for example the examination of tensile properties, it is recommended that the tests on both reference and aged material be performed at the same time, that is after the exposure of the latter to the ageing conditions.

The ageing conditions shall be chosen from the following alternatives which should be appropriate to the material under test. It is recommended that materials differing in chemical composition should not be aged in the same enclosure.

5.2 Dry heat ageing

5.2.1 Temperatures

Polyolefin 70°C

Latex 70°C or 100°C

Polyurethane 125°C or 140°C

NOTE — The use of the non-standard temperature of 140 °C is included for the following technical reason: the temperature of the ageing test should be as high as possible to enable results to be obtained in the minimum time, but above this critical temperature the changes which occur when polyurethane foam is tested are not those which are found in service, so that the ageing test will no longer discriminate between foams of different behaviour in service.

5.2.2 Duration of ageing

Use 16 h, 22 h, 72 h, 96 h, 168 h, 240 h or some multiple of 168 h, with a tolerance $\pm 5\%$, but not more than ± 4 h.

5.3 Humidity ageing

5.3.1 Humidity

Use 100 % relative humidity or saturated steam.

5.3.2 Temperatures and duration of ageing

Material	Conditions
Polyurethane (all types)	85 °C for 20 h or 105 °C for 3 h
Polyurethane (polyether only)	120 °C for 5 h

Tolerance on temperature: ± 2 °C

Tolerance on duration of ageing: $\pm 5\%$ but not more than ± 2 h, the time being measured from the time when the air in the vessel has been replaced by water vapour or steam.

NOTE — In this test for resistance to hydrolysis, the use of the non-standard temperatures of 105 °C and 120 °C is included for the following technical reasons: 105 °C is used because this temperature requires the use of a closed vessel so that control of the conditions is better than at the alternative of 100 °C; 120 °C is used because much experimental evidence has been accumulated at this temperature, but little or none at the alternative of 125 °C. Until these background data are collected it is not considered possible to change to 125 °C.

5.4 Reconditioning

After exposure to the ageing conditions, test pieces undergoing humidity ageing shall be dried at $70\text{ °C} \pm 2\text{ °C}$ for 3 h per 25 mm of thickness, subject to a minimum of 3 h. The humidity-aged test pieces shall then be reconditioned in the atmosphere specified in 4.2 for 3 h per 25 mm of thickness. Dry-heat-aged test pieces shall merely undergo the reconditioning procedure.

After reconditioning, the properties of the aged test pieces shall be tested.

6 Expression of results

6.1 Calculation

The percentage change in the property being examined is given by the formula

$$\frac{\bar{X}_a - \bar{X}_0}{\bar{X}_0} \times 100$$

where

\bar{X}_0 is the average value of the property before ageing;

\bar{X}_a is the average value of the property after ageing.

6.2 Format

The value of the percentage change shall be stated, followed by the test condition in parentheses, in order time, temperature and method.

EXAMPLE

Value % (16 h, 70 °C, dry heat).

7 Test report

The test report shall contain the following information:

- a) a reference to this International Standard;
- b) a description of the material;
- c) the procedure and conditions used;
- d) the average final value of the property;
- e) the percentage change in property, expressed as indicated in clause 6;
- f) the date of the test;
- g) any deviations from this International Standard.

Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption

PB VWL 709

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0 Circulation
Plant 50 VWL Teams, VWK
Plant 54 QWO
Plant 67 QST

1 Objective
The purpose of this analytical method is to determine emissions from materials used in vehicle interiors.

2 Scope
DaimlerChrysler, Mercedes-Benz product line

3 Terms
Emissions, interior trim materials, vehicle interior air, thermodesorption analysis (TDSA), VOC value, Fog value.

4 Responsibilities
PWT/VWL, Organic Analysis Team

5 Description
Vehicle interior materials are characterized according to the type and quantity of organic substances that can be stripped from them. Two cumulative values are determined to this end, from which the emission of volatile substances (VOC value) and the condensable content (fog value) can be estimated. Individual emission substances are also identified. During analysis the samples are thermally desorbed and the emissions separated out by gas chromatography and detected by mass spectroscopy.

6 Applicable documents
DBL 8585, List of MAC and BAT values (DFG)

7 Appendices

1. Notes on weighed amounts and preparation of samples	File names PBVWL709Anl1.doc
2. Production of paint samples	PBVWL709Anl2.doc
3. Excel report template	PBVWL709Anl3.doc
4. Sketch of thermodesorption analysis	PBVWL709Anl4.doc
5. Sample chromatogram for control test mixture	PBVWL709Anl5.doc
6. Limiting/target values	PBVWL709Anl6#2.doc

Issued : 2007-01-11	Author:	Approved:
Replaces : 2000-07-19	Kante	Dr.Munz
File : PBVWL709#2_eng		
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Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption

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Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption

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1 General notes, definitions and organization of contract

1.1 Materials to be tested, relevant vehicle interior area in relation to emissions

All materials that can contribute to emissions in the vehicle interior must be tested. Examples include emissions from textiles, carpets, adhesives, sealants, foams, plastic components, films, leather, interior paints and composite materials. The relevant vehicle interior area in relation to emissions comprises all areas that are linked to the passenger compartment either directly or by air contact. It also includes the luggage compartment, air-conditioning and heating systems, spaces behind trim, etc.

If there is no difference in the composition of different samples of a material or if the difference in formulation is not expected to influence emissions, it is sufficient to examine representative samples of this component family.

Responsibility for the accuracy of the assumption that emissions are identical lies with the supplier. In case of doubt he should contact his upstream supplier.

For the first sample at least, a laboratory authorized by DaimlerChrysler must perform the VOC/fog analysis. The supplier must send the results to DaimlerChrysler (see section 3.4.5).

1.2 Thermodesorption analysis

In thermodesorption analysis (TDSA) small quantities of material are heated in a glass tube under defined conditions, the volatile substances emitted during the process are transferred to a gas chromatograph in an inert gas stream, where they are first cryofocused at -150°C in the cryogenic trap (liner) of a temperature-programmable evaporator¹.

At the end of the curing phase the liner is quickly heated to 280°C . The focused substances evaporate, are separated out in the gas chromatographic analytical column and then detected by mass spectroscopy.

Appendix 4 provides a schematic view of the thermodesorption analysis equipment.

A semi-quantitative determination of the emissions, expressed as mass ppm², can be obtained by calibration with reference substances. Toluene and n-hexadecane are used as reference substances for VOC analysis and the fog value respectively. Unknown substance peaks can be identified from the mass spectra and the retention time.

¹ Here: = Cold Injection system (CIS) = Temperature-programmable injector for gas chromatograph

² ppm = parts per million = μg of substance per g of weighed portion that are stripped + detected under these conditions. It is not a measure of content.

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1.3 VOC value³ (according to PB VWL 709)

The VOC value is the sum of volatile to moderately volatile substances. It is calculated as toluene equivalent.

In the method described here, substances in the boiling or elution range from pentane (C5) to eicosane (C20) or thereabouts are identified and evaluated. It is assumed that these substances can be detected from an analysis of the vehicle interior air.

Determination is performed by curing the sample for 30 minutes at 90°C . The VOC value is measured as a double value.

The higher of the two values is cited as the result.

1.4 Fog value

Following VOC analysis the fog value is determined by leaving the second sample in the desorption tube and curing it for a further 60 minutes at 120°C .

The fog value is the total of highly volatile substances that elute from n-hexadecane from the retention time onward. It is calculated as hexadecane equivalent.

Substances with boiling points up to at least n-alkane C32 are detected.

These substances can readily condense at room temperature and make a substantial contribution to the fogging coating on the windshield.

The limits for the VOC and fog range have been established by convention. They have been derived empirically from numerous analyses of vehicle fogging condensates.

According to these analyses, fogging consists primarily of substances that boil above around 280°C (boiling point of n-hexadecane = 286°C).

1.5 Evaluation of emitted substances

Reference is made to the latest list of MAC values⁴ and to DBL 8585 in order to evaluate the toxicity of the substances identified. Substances listed in the following categories should be rated as critical:

Category	Classification
Carcinogenic	K1, K2, K3 A, K3 B
Pregnancy	A, B
Mutagenic	1, 2, 3 A, 3 B
Allergic effect	H, S

³ VOC value = volatile organic compounds

This VOC value refers exclusively to the method described here and is not comparable with VOC values obtained using other methods.

⁴ List of MAC and BAT values, issued by: Deutsche Forschungsgemeinschaft, Wiley-VCH-Verlag

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If substances of this type are detected, they must be explicitly identified in the analysis report.

Substances that are assumed or known to be potentially harmful due to their physiological properties (e.g. odor, irritation to mucous membranes) must also be rated as critical.

The same applies to substances that can be regarded as precursors of other critical compounds or that are known allergens, e.g. carcinogenic nitrosamines can form from aliphatic secondary amines.

Limiting values for VOC, fog and individual substances are set out in Appendix 6.

1.6 When is VOC/fog analysis required?

1.6.1 Sample approval/development

The relevant supply specifications state whether material testing is necessary along with any requirements that exist.

Generally speaking, the results of the thermodesorption analysis must be submitted together with the first sample test report for first and new sample approvals.

For coordination purposes the supplier must submit a VOC/fog result from the Institut Fresenius⁶ for the **first sample test report**.

For the sample approval of materials comprising various components, analyses already arranged by upstream suppliers can be submitted.

In the context of the preliminary development of materials, a decision can be made by agreement with the team responsible for the material regarding the stage of development beyond which an analysis is reasonable.

1.6.2 Standard monitoring

In the context of standard monitoring of approved products, a simple determination of the overall VOC and fog value, in other words no analysis of individual peaks, is all that is required. This must be arranged by the supplier at appropriate test intervals and documented. A visual comparison with the approved chromatogram is sufficient to check for any substantial changes, e.g. additional new substances.

⁶ Address:

Institut Fresenius, Chemische und Biologische Laboratorien GmbH
Dr. Krüger
Hauert 9
44227 Dortmund
Germany
Tel. +49 (0)231/759960

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1.6.3 Formulation changes

New sample approval is required under all circumstances in the event of changes to the formulation that could worsen emissions.

1.6.4 Complaints

In the event of complaints about materials relating to the question of emissions, thermodesorption analysis may help to identify the cause.

Details of a complaint analysis should be agreed with the DaimlerChrysler team in charge.

1.7 Timing of sampling/preparation/dispach

The time at which a sample is taken for analysis must be chosen such that the age of the material corresponds to the shortest possible delivery time for the component to the DC final assembly plant.

Example:

A foamed material is generally delivered to the car plant within 2 to 12 days after foaming. Analysis must therefore be performed on a foam sample that has been allowed to evaporate for a maximum of 2 days.

The worst-case scenario must always be assumed.

A representative sample of size DIN A5 or thereabouts is taken for analysis. It must not become contaminated. Each sample is completely wrapped in an airtight package comprising two layers of thick aluminum foil (30 µm), the edges of which are folded several times. The sample is also sealed in a polythene bag and can then be sent to the laboratory. It is then stored at a maximum of -18°C until it is analyzed.

Further details of the handling of the material for analysis and the preparation of the sample are provided in Appendices 1 + 2.

Appendix 1: Determining the weighed amount of different material samples.

Appendix 2: Specifications for the production of paint films.

1.8 Presenting the results of the analysis

The contracted laboratory prepares a written analysis report containing the VOC and fog value together with a list of the substances detected. The substances are quantified and compared with the current MAC list.

The component supplier sends DaimlerChrysler the written laboratory report, comprising the GC report, chromatograms for the VOC and fog analysis, and all raw data from the analysis (on CD-ROM), for inspection.

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2 Analysis parameters

2.1 Instrument system

The analytical method described in this report was performed with the following instrument system:

<u>Instrument</u>	<u>Model/manufacturer</u>
Thermodesorption system	TDSA (with auto sampler), Gerstel, glass desorption tube, external diameter = 6 mm, internal diameter = 4 mm
Gas chromatograph (GC)	HP6890 with electronic pressure regulation, Agilent (Hewlett Packard)
Cryogenic trap	Cold injection system KAS 3, Gerstel, glass liner: smooth type, filled with deactivated quartz wadding (cat. no. 842010)
Mass spectrometry detector (MSD) Evaluation software	HP5972A, Agilent (Hewlett Packard) Chemstation G1701BA MS Excel 97, Wiley275/Nist MS spectra library

Notes:

Attention

Transferability of results cannot be assumed if different thermodesorption/GC systems are used. It must be checked in each case.
In some circumstances the quantity emitted is substantially dependent on the constructional features of the individual analytical instrument system. For example, the geometry of the sample chamber, the length of the heated zone, the length of the transfer line, the type of pneumatic regulation or different flow conditions, may influence the result.

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2.2 Device parameters for the VOC analysis run

2.2.1 Thermodesorption unit (TDSA) parameters for the VOC analysis run

Sample mode	Sample removal
Flow mode	Splitless ⁶
Initial temp.	20°C
Delay time	1 minute
1 st rate	60 K/min.
1 st final temp.	90°C
1 st final time	30 minutes
Transfer line to CIS	280°C
GC run time	67 minutes

2.2.2 Cryogenic trap (cold injection system, KAS 3) parameters for the VOC analysis run

Flow mode	Split 1:30
Initial temp.	-150 °C
1 st rate	12 K/sec
1 st final temp.	280°C
1 st final time	5 minutes
Equilibration time	1 minute

2.2.3 Gas chromatograph (GC) device parameters for the VOC analysis run

Transfer line to MSD	280°C
Carrier gas	Helium 5.0, post-purified
Flow rate	1.3 ml/min.
Pneumatics (EPS)	Constant flow mode
Analytical column	50 m x 0.32 mm, 0.52 µm
	5% phenylmethyl siloxanes
	HP Ultra 2 (19091B-115)
Oven temperature program:	40°C, 2 min. isothermal,
	3 K/min. to 92°C
	5 K/min. to 160°C
	10 K/min. to 280°C.
	(Total run time: approx. 59 minutes) 10 min. isothermal

2.2.4 Mass spectrometer settings (MSD) for the VOC analysis run

Start of data recording	After 3.0 minutes
Calibration of mass axis	Standard spectra autotune
	(measured at oven temp. of 100°C)
Scan mode (low/high mass)	29-280 amu, at 3.1 scans/s
MS threshold	100

Note: The chromatographic integration conditions must be selected so that 1 ppm peaks can be detected reliably.

⁶ For technical reasons a forced split flow of approx. 3 ml/min nevertheless occurs here.

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2.3 Device parameters for the fog analysis run

2.3.1 Thermodesorption unit (TDSA) parameters for the fog analysis run

Sample mode	Sample removal
Flow mode	Splitless
Initial temp.	20°C
Delay time	1 minute
1 st rate	60 K/min.
1 st final temp.	120°C
1 st final time	60 minutes
Transfer line	280°C
GC run time	57 minutes

2.3.2 Cryogenic trap (cold injection system KAS 3) parameters for the fog analysis run

Flow mode	Split 1:30
Initial temp.	-150 °C
1 st rate	12 K/sec
1 st final temp.	280°C
1 st final time	5 minutes
Equilibration time	1 minute

2.3.3 Gas chromatograph (GC) device parameters for the fog analysis run

Transfer line to MSD	260°C
Carrier gas	Helium 5.0, post-purified
Flow rate	1.3 ml/min.
Pneumatics (EPS)	Constant flow mode
Analytical column	50 m x 0.32 mm, 0.52 µm 5% phenyl/methyl siloxanes HP Ultra 2 (19091B-115)
Oven temperature program:	50°C, 2 min. isothermal, 25 K/min. to 160°C 10 K/min. to 280°C,
(Total run time approx. 48 minutes)	30 minutes isothermal

2.3.4 Mass spectrometer settings for the fog analysis run

Start of data recording	After 12.5 minutes
Calibration of mass axis	Standard spectra autotune (at oven temp. of 100°C)
Scan mode (low/high mass)	29-370 amu, at 2.3 scans/s
MS threshold	100

The chromatographic integration conditions must be selected so that 1 ppm peaks can be detected reliably.

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3 Method of analysis

3.1 Cleaning the glass desorption tubes

Only glass tubes that are completely free from contamination may be used. Even brand-new desorption tubes must be thoroughly cleaned before being used for the first time. The tubes must be cleaned by storing them for several hours, ideally overnight, in an alkaline cleaning solution⁷. They must then be rinsed thoroughly, first under hot running water for at least one minute, then with demineralized water. The tubes are then dried in a drying oven (approx. 45 minutes at 105°C) and stored free from contamination (wrapped in aluminum foil in an airtight package) until use.

3.2 Testing the system

The function of the instrument system is tested by analyzing a standard control solution within the sample series (see 3.2.1). The standard control solution contains non-polar, polar basic and acid components that would display a noticeable peak tailing even with low adsorption effects. This process can also be used to check for substance losses due to leaks. Peaks occurring in dose succession, such as o-xylene and n-nonane, can be used to check the separation efficiency of the chromatographic column. These two substance peaks must be virtually baseline-separated under the chosen chromatographic conditions.

The performance of the mass spectroscopy detector is checked by means of mass and sensitivity tuning (standard spectra autotune in the case of HP instruments), and the specifications required by the manufacturer must be achieved. An air/water check must also be performed to test the integrity of the entire system.

All substances in the control mixture must be clearly identified in the mass spectra library (e.g. Wiley 275) during the search run.

The TDSA/GC system must also be checked for possible memory effects by performing a dummy run with an empty desorption tube at least before every sample series. If negative effects such as severe peak tailing, disruptive dummy run peaks or significant loss of substance occur, the system must be cleaned. The GC column, CIS liner, transfer line or seals may need to be replaced.

We recommend documenting the results of the control run for each sample series as part of quality control procedures (control card). The peak area ratios, concentrations as toluene equivalents and retention times can be used as control quantities.

3.2.1 Preparing the control solution

⁷ The alkaline laboratory glass cleaner SODOSIL RA8 (Riedel-deHa7n) has proven effective.

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The following substances dissolved in methanol have proven to be suitable for use as the system control (listed in elution sequence under VOC conditions):

Table 1 Control mixture

benzene	2-ethylhexanol-1
n-heptane	n-undecane
toluene	2,6 dimethylphenol
n-octane	n-dodecane
n-butyl acetate	n-tridecane
p-xylene	n-tetradecane
o-xylene	dicyclohexylamine
n-nonane	n-pentadecane
n-decane	n-hexadecane

220 ± 20 mg of each component are weighed into a glass vessel (e.g. 5 ml roll-edged glass) to an accuracy of 0.1 mg. Approx. 100 mg of this mixture are transferred to a 50 ml measuring flask and weighed (weighing accuracy ± 0.1 mg). Methanol (p.a.) is then added to just below the calibration mark on the measuring flask, the flask is closed and carefully shaken until all solvent droplets have fully dissolved in the methanol. The measuring flask is then filled up to the calibration mark and shaken again.

4 µl of this solution are then injected into a Tenax desorption tube for the control run (as described in section 3.3.2).

This means that the desorption tube contains approx. 0.45 ± 0.05 µg of each substance.

The retention times for the n-alkanes present in this mixture are a suitable reference point for determining the retention index of unknown substance peaks and can therefore be used as an additional check for MS identification during the sample runs.

3.2.2 Stability of the control solution

Apart from the n-butyl acetate component, the control solution can be kept for several weeks if stored correctly (refrigerated at 8°C maximum). Butyl acetate hydrolyzes noticeably within a few days, however. An additional butanol and acetic acid peak occurs in the chromatogram and the butyl acetate peak becomes correspondingly smaller. In this case the control solution must be repeated with a fresh batch in order to evaluate the butyl acetate peak.

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3.3 Calibration

Calibration is performed using the external standards method.

This method involves charging separate desorption tubes containing Tenax TA with the individual calibration solutions.

3.3.1 Calibration solutions

Two calibration solutions are required:

1. For the VOC analysis approx. 0.5 µg/µl toluene (p.a.) in methanol (p.a.)
2. For the fog analysis approx. 0.5 µg/µl n-hexadecane (p.a.) in methanol (p.a.)

Approx. 25 mg (accuracy to ± 0.1 mg) of toluene or n-hexadecane are weighed into a 50 ml measuring flask, the measuring flask is filled with methanol to just below the calibration mark, closed and shaken well. The flask is then topped up with methanol to the calibration mark and shaken again.

The calibration solutions can be stored in a cool place for up to 3 months.
Guaranteeing the accuracy of the concentration is part of the laboratory's quality control procedure.

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3.3.2 Charging the calibration or control solution onto Tenax

A desorption tube filled with Tenax TA is connected to an injection device guaranteeing a controlled flow of inert gas (helium 5.0) through the tube while the calibration solution is being added.

Models consisting of septum screw fittings from worn-out GC injectors or a cold injection head fitted with an adaptor and no septum (Gerstel) have proven effective. The advantage of the latter design is that the dead volumes are relatively low, so fewer losses can occur.

A simple adjustable flowmeter should be connected upstream of the injection device to control the helium flow.

A gas meter for controlling the overall volume passing through the injection device and for checking the integrity of the system must be connected downstream of the injection device.

The flow rate should be set to approx. 0.7 ± 0.3 l/min, and the total flow quantity should be around 2.5 – 3 liters. The methanol matrix fed into the system is largely removed, whereas toluene or hexadecane remain on the Tenax.

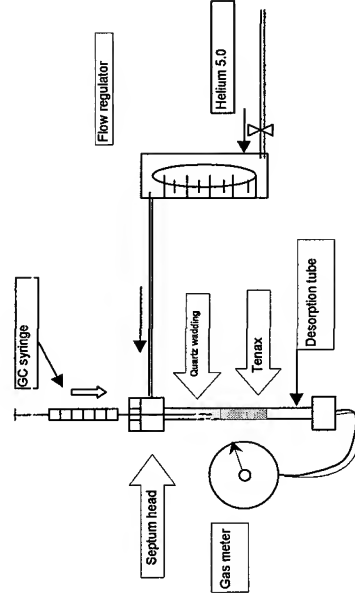


Fig. 1 Equipment for charging the calibration solution

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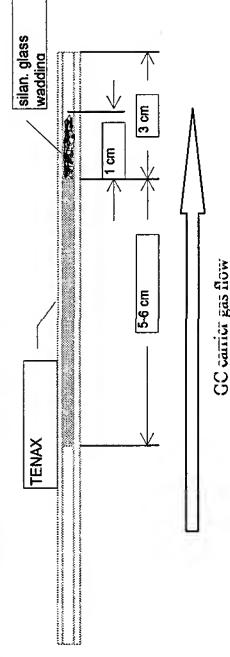
3.3.2.1 Tenax desorption tube:

The Tenax packing must be inserted into the tube in such a way that it can be completely covered by the heating zone of the desorption oven.

For the tubes in the Gerstel TDSA instrument the Tenax packing should be around 5-6 cm in length.

A gap of approx. 3 cm must be left between the Tenax packing and the end of the tube on the transfer line side to prevent the transfer line from protruding into the packing. A plug of deactivated (silanized) glass wadding measuring approx. 1 cm in length, into which the calibration solution is injected, is placed on top of the Tenax layer.

Fig. 2 Tenax packing in the desorption tube



After bringing the calibration solution up to room temperature, 4 µl are drawn up with a 10 µl GC syringe, ensuring that the solution is free from bubbles, and slowly (over approx. 15 seconds) injected into the plug of glass wadding. The inert gas flow is switched on during this process.

Notes:

1. To avoid losses it is advisable to inject the calibration solution directly into the glass wadding plug. Otherwise sizeable fluctuations in the measured values are likely.
2. Tenax can alter over time depending on usage. The quality of the Tenax tubes must be checked by suitable means (e.g. visual check + dummy run), if necessary the packing should be replaced.

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3.3.3 Analysis parameters for the calibration and control solution

3.3.3.1 Thermodesorption unit (TDSA) parameters for the calibration run

Sample mode	Sample removal
Flow mode	Splitless
Initial temp.	20°C
Delay time	1 minute
1 st rate	60 K/min
1 st final temp.	280°C
1 st final time	5 minutes
Transfer line to CIS	280°C

3.3.3.2 Cryogenic trap (cold injection system, KAS 3) parameters for the calibration run

Flow mode	Split 1:30
Initial temp.	-150 °C
1 st rate	12 K/sec
1 st final temp.	280°C
1 st final time	5 minutes
Equilibration time	1 minute

3.3.3.3 Gas chromatograph parameters for the calibration and control run

The same parameters are used for toluene calibration and analysis of the control mixture as for the VOC sample run. Only data recording begins later, after approx. 5.5 minutes, in order to mask the methanol peak.

Hexadecane calibration is performed under the same GC conditions as the fog analysis run.

The GC runs can be shortened relative to the sample runs by interrupting the oven temperature program following elution of the calibration substances.

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3.4 Sequence of sample analyses

3.4.1 Cutting the samples to size and weighing them into the desorption tubes

For each sample two tubes are filled with the weighed amount specified for the material:

Tube A:	First VOC analysis run
Tube B:	Second VOC analysis run followed by fog run.

Prior to being weighed, deep-frozen samples must be brought back to room temperature before opening the PE bag to prevent condensation of atmospheric moisture.

The weighed amount of the samples depends on the type of material being tested. It is generally between 10 mg and approx. 50 mg (see Appendix 1).
Required accuracy: ± 0.1 mg.

Weighed amount of sample:
Weighed amounts of specific materials are listed in **Appendix 1**.

Given the variety of possible sample materials, it is impossible to provide a universal specification for the sizing of samples.

When cutting the sample to size, the aim should be to obtain as coherent and "plane" a size as possible. The aim is **not** to obtain the largest possible surface area by reducing the size. The following procedure should be taken as a guideline:

The desorption tube has an internal diameter of 4 mm which, because of the thickness of the sample, cannot be fully utilized. The temperature-controlled zone of the tube and hence the maximum sample length is around 4 cm.

In order to insert as large pieces as possible, maximum use should first be made of the width of the sample tube when cutting the sample to size. The maximum sample width is generally around 3 mm. The length and thickness of the sample are variable and governed by the specified weighed amount (Appendix 1). It is preferable to cut the sample slightly on the long side and reduce the thickness accordingly.

The sample size should be stated in the report (e.g. L x B x H = approx. 15 x 2.8 x 0.7mm).

A special procedure involving dried films applied to aluminum foil is used for paints and adhesives (see Appendix 1-2).

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3.4.2 Calibration run, determining the calibration factors (response factor)

At least two Tenax desorption tubes for each sample series are charged with the toluene or hexadecane calibration solution (see section 3.2) and the areas of the calibration peaks determined.

The response factor is calculated as the quotient of the absolute mass (in µg) of toluene or hexadecane that was injected into the tube and the resulting peak areas in each case.

Equation 1

$$Rf = \frac{\mu\text{g toluene (C16)}}{\text{peak area}} \times 1000000$$

3.4.3 Quantitative chromatographic evaluation

The total area of all of the substance peaks occurring in the chromatogram (excluding artifacts) is determined first.

The integration parameters for the chromatography software must be set so that peaks with a concentration of ≥ 1 ppm are still detected reliably.

If the chromatogram includes so-called "oil mountains", consisting of coherent chemically identical isomer mixtures, these are integrated as one peak, in which the baseline is laid from the start to the end of the "mountain". If additional and clearly identified peaks of other substance classes occur in this zone, they must be integrated and specified separately.

In order to calculate the concentration, the individual peak areas are multiplied by the response factor (see section 3.4.2)

for toluene, in the case of VOC analysis,
for hexadecane, in the case of fog analysis

and divided by the appropriate weighed amount of sample:

Equation 2

$$\text{Emission [ppm]} = Rf(\text{toluene/C16}) \times \frac{\text{Peak area [counts]}}{1000 \times \text{weighed amount of sample [mg]}}$$

The total concentration from the VOC run calculated as toluene equivalent gives the VOC value. The total concentration from the fog run calculated as hexadecane equivalent gives the fog value.

If the VOC results deviate by more than 20% relative to the mean value, a repeat analysis, including a fog run, must be performed. Both VOC values must be stated in the test report, but the analysis with the higher value is used for evaluation.

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3.4.4 Qualitative analysis

The individual peaks (> 1 ppm) are classified on the basis of their mass spectra and – if available – their retention indices (from the literature or reference analyses). Every MS search run result must be checked for plausibility before being transferred into the results table.

If a substance cannot be clearly identified, a possible suggestion marked with a question mark or a reference to the substance class can be given, provided that appropriate reference points (e.g. typical mass fragments) permit such conclusions to be drawn.

The following convention should be followed for indicating the varying reliability of the substance classification:

Example of notation	Explanation
Toluene, methyl benzene	Mass spectrum and retention of the reference substance are virtually identical (classed as a very reliable identification)
? 1,1-bis (p-toluy)ethane 210 195 179 104	=> Preceding question mark: No definite classification can be made from mass spectra or retention, but this substance is regarded as a possibility (very similar). Significant mass fragments are cited (=> Question mark + name of substance class)
? Alcohol, 31 57 85	Typical fragments or known fragment samples suggest the substance class
? 54 76 99 109	No conclusions can be drawn about the compound
Isomeric paraffin fraction, boiling range "C16-C26"	In the case of "oil mountains" the substance class should be given as the substance name and the approximate boiling range stated, relative to n-alkanes. The retention-time of the mountain maximum should be entered in the column headed "Retention time"
Cyclohexanone + ?	An identified peak is superimposed by one or more unknown substances
Artifact	Peak that cannot originate from the sample or that has been generated in the system

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3.4.5 Results reports/documentation

The chromatography results are transferred to an Excel table containing, as a minimum, the following information about the tested sample:

Header area	Results area
> Exact name of the material tested (material, batch)	> Retention time
> Component name	> Substance name
> Manufacturer's/supplier's name	> CAS number
> Date of manufacture of material	> Percentage of peak
> Analysis date	> Concentration [ppm]
> Weighed amount [mg]	> Comments on peak
> Approximate sample size	> VOC (fog) value
> Part no.	> Second VOC value
	> Comments on analysis

A corresponding Excel template is provided in Appendix 3.

Note regarding the substance name field

Various naming conventions for a substance, such as are commonly suggested in MS libraries, can be copied over directly, but the substance name field should not be overloaded with too many, generally superfluous, names.
It is sufficient to state 1 to 3 "conventional" names in addition to the CAS name.

The chromatograms for the VOC/fog determination and associated substance lists (Excel printout) must be attached to the results report. The full set of analytical data must be supplied on a CD-ROM. It should include:

- > 2 raw chromatogram data files for the VOC determination ⁸
- > 1 raw chromatogram data file for the fog determination
- > Raw chromatogram data files for the dummy runs
- > Raw chromatogram data files for the calibration and control runs ⁹
- > Excel files containing the detailed results of the VOC/fog analysis ⁹

⁸ All raw chromatogram data files must be able to be read by Chemstation MSD software (G1701BA)
⁹ Using the DC Excel template (see Appendix 3)

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Note:

1. The Agilent Chemstation software transfers the chromatography results to the Excel data format using DDE file transfer. This process and the subsequent calculation of the concentration values can be automated using appropriate Chemstation and Excel macros.
2. For the first sample approval, conventions must be complied with in order to ensure that data can be exchanged with DC systems. Particular information has to be entered in defined Excel cells, for example. The contracting laboratory may need to contact DC for details.

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4 Validation characteristics

4.1 Scattering of measured values for samples

Reproducibility depends on, amongst other things, the quality of the sample matrix, its composition, volatility and the diffusion properties of the emitters. The result also depends on whether reproducible surfaces can be produced during preparation of the samples. This can be more difficult in an open-pore foam, for example, than in a compact plastics sample.

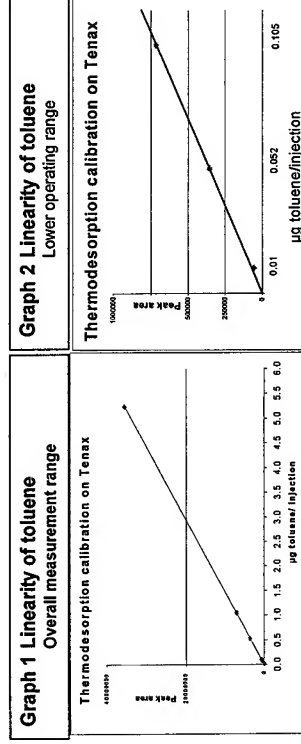
Experiences with numerous measurements of various materials show that a reproducibility of < 15% is generally achieved for the VOC value.

4.2 Limit of determination/linearity

The matrix-independent performance of the overall system is illustrated below by reference to the example of the linearity of toluene: defined amounts of toluene were analyzed according to section 3.3 and the statistical properties determined from the peak areas obtained.

Graph 1 demonstrates the linear progression of the toluene response up to a high concentration zone (5 µg would correspond to approx. 150 ppm in a 30 mg sample).

Graph 2 illustrates the linear progression of three lower measuring points.



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The following correlation values are obtained from the overall data for this series of measurements:

$$Y = a^1 X + a^0$$

$$a^1 = 6761000 \pm 48000$$

$$a^0 = 10300 \pm 98000$$

$$\text{Correlation coefficient: } r = 0.99998$$

For the lower working range (VB = 95%)

Detection limit: 0.005 µg
Determination limit: 0.02 µg

Note:

1. The statistical characteristics were calculated according to DIN 38402 ¹⁰.
2. The determination and detection limits established here do not entirely reflect the conditions for an actual sample measurement. They are provided simply to help understand the minimum performance requirements for the analytical system.

4.3 Scattering and recovery of toluene

The toluene content was calculated from the control standard charged onto Tenax. The following measured values were obtained:

Number of measured values:	N = 20
Number of measurement series:	6
Standard deviation	5.4 %
Mean recovery value (Actual/nominal value x 100)	102 %
Maximum recovery value	117 %
Minimum recovery value	85 %

The series of measurements was conducted over a period of approximately 6 weeks.

¹⁰ Determined with: SOS software for statistical quality control of analytical data, PERKIN-ELMER

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5 Possibilities for error, known problems

5.1 Sample preparation

When preparing the samples it is important to avoid any contamination or unnecessary heating of the samples. The samples must not be touched with the fingers or cut using heat-generating cutting techniques (e.g. high-speed circular saws). The use of scalpels, tweezers, cork borers or scissors or pliers for harder samples is usually sufficient.

Cutting, weighing and transfer of the sample into the desorption tube must be done quickly. The charged desorption tube must be placed immediately into the autosampler feeder to avoid emission losses.

The specific surface area of the sample also has a significant influence, so its preparation should be made as reproducible as possible. Generally speaking, a higher level of emissions is obtained with a larger sample surface area. However, since the VOC/fog value always relates to the weighed amount, not to the surface area, and substances can behave differently in different matrices, this correlation is not entirely linear.

5.2 Incorrect substance identification

Misinterpretations can sometimes occur if substances cannot be separated or can only just be separated with the chosen analysis parameters. In particular, if substances with large concentration differences are eluted almost together, the smaller peak can easily be overlooked.

Examples (with no claim to completeness):

Ret. time (VOC)	Substances	Mass fragments	Comments
6.5 min.	Benzene/ methylcyclopentane/ butanol	78/69/ 31	
	Vinyl acetate /butadiene-1,3		Same mass spectra > risk of confusion! Distinction: ret. time is approx. 3.1 min. for butadiene-1,3 and approx. 4.2 min for vinyl acetate
13.9 min	o-xylene Cyclohexanone Butyl acrylate	91 98 73	Small amounts of cyclohexanone can sometimes be detected if the p/m xylene MS is subtracted from the o-xylene MS.
12.7 min	p+m-xylene Acetamide, N,N-dimethyl	91 44 72 87	
	Methoxypropyl acetate	43 58 72 87	

The guideline mass fragments listed here can also be used to check the particular substance by means of ion extraction.

5.3 Known Problems with the cold injection system (CIS, Gerstel)

It has been noticed that highly volatile substances (including toluene) can leak if the CIS liner is not adequately packed with silanized glass wool. This then has an influence on the calibration that is not immediately obvious.

If the semi-volatile substances display small pre-peaks during analysis of the control mixture (from around decane onwards), there is a strong possibility that a leak has occurred.

=> Remedy: pack additional glass wool loosely into the liner.

Increasing the amount of glass wool can also increase the peak areas and so produce better sensitivity. It also means that when the liner is changed the system will have to be recalibrated.

F Attention:

If liners are packed too tightly, the flow of carrier gas may not be able to be sustained in some circumstances (pressure increases).

5.4 Samples with a high water content

If very large quantities of water can be emitted from samples, there is a possibility that the liner, which has been cooled to -150°C, will freeze partially or entirely during desorption.

=> Result:

Values too low or analysis aborted completely (pressure increase too great).

This effect occurs in some circumstances in the case of samples containing leather or natural fibers.

=> Remedy: reduce weighed amount.

Appendix 1 to the DaimlerChrysler Test Instructions PB VWL 709**Weighted amounts of various materials for thermodesorption analysis**

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

Unless otherwise specified, the standard weighed amount of samples is 30 ± 5 mg. The weighed amount generally applies to strip-shaped samples cut to size with a scalpel. The weighed amount has been specified for the following materials:

Material type	Weighted amount mg	Comments
Foam	15 ± 2	Material should be placed in the tube as loosely as possible and without being compressed. The influence of the weighed amount can be very high in the case of foams, which is why such narrow margins are necessary. Sampling point: on the surface of the foam (due to the possible influence of release agents).
Fiber composites (SMC, carbon fibers, etc.)	60 ± 20	Thicker sheets are usually split through the layer
Film-type samples	30 ± 5	Weight out as individual strips where possible
Leather	10 ± 2	To obtain a more realistic measure of the influence of the wear surface of the leather and to take into account the effects of any protective coating that may have been used, part of the fabric side must be removed in the case of thicker leather samples. This also reduces the risk of the cryogenic trap freezing in the case of leather samples with a high water content. The following also applies until further notice: If the cryogenic trap still freezes when the method set out above is used, the weighed amount can be halved.
Paints	Calculated as shown	Paints are applied to aluminum foil and dried according to standard conditions. Film thickness: 50 ± 5 µm. Strips measuring 30mm x 3mm are cut from the film, weighed out and analyzed (the basic weight of the aluminum has to be deducted from the weighed amount). See also continuation sheet 2.
Adhesives/ composites etc.	30 ± 5	Where possible, weigh out in the form of strips of film of the same thickness used for the application (applied to aluminum foil)

Reasons for deviating from the specified weighed amounts must be logged.

Appendix 1 to the DaimlerChrysler Test Instructions PB VWL 709**Weighted amounts of various materials for thermodesorption analysis**

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

Procedure for multilayer sandwich samples:

In order to keep costs to a minimum, it is permissible to analyze multilayer sandwich constructions together.
If the individual layers are relatively thick (over approx. 0.5 mm), the material in each layer should be analyzed separately. This is also useful in order to be able to allocate the emitted substances accordingly and to introduce targeted corrective action.
In addition, the results obtained are more reliable as the emission values can be related to the relevant individual material and the ratio of the thickness of the various layers can be disregarded during preparation of the samples (\Rightarrow better comparability for material development).

If uncertainties are likely to arise as a consequence of the sample construction, each component must be analyzed separately (e.g. thin adhesive film on the surface of thick layers of foam).

In isolated cases it may be useful and possible to analyze the entire cross-section of the sample. This is done by punching out a core sample (diameter = 3 mm) from the entire cross-section of the sample and cutting it in half lengthways. Half core samples from different places are analyzed.

Other methods of sample preparation can also be established if necessary for specific components. The chosen method of sample preparation must be stated in the results report.

Appendix 2 to the DaimlerChrysler Test Instructions PB VWL 709

Production of paint films for thermodesorption analysis

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

To ensure comparability and consistency of measured values, the paint drying conditions must be defined and matched as closely as possible to standard production. Standard conditions in the paint shop must also correspond to the instructions for use issued by the paint supplier.

The following procedure has been established for the production of paint films:

- › The paint is sprayed onto a clean sheet of aluminum foil of size DIN A5 and a maximum of 30 µm thick. Dry film thickness: 50 µm ± 5 µm (deviating from standard production if necessary).
- › After being allowed to dry briefly (similar to standard production), the wet paints are stored in a laboratory drying oven. The exact stoving temperature must be measured using a thermocouple positioned at the same height as the sample, and documented.
- › Different types of samples must not be placed in the drying oven at the same time. To avoid contamination, the oven must be heated for at least two hours at 200°C before use. Once preheated to the reference temperature (± 1.5 K), the oven may be opened only briefly to insert the samples.
- › Loading the oven:
 - Samples should be loaded on one rack level only (middle rack level)
 - Oven operation: Partial air circulation at maximum circulation rate (> 10 l/(min))
10 ± 5 % fresh air supply
 - Oven load: 1 ± 0.2 l/m

Example:

- a. Oven volume = 0.13 m³
- b. Paint area = 0.12 m² (equivalent to 4 DIN A5 sheets)
- c. Oven load = 0.12 m³ / 0.13 m³ ≈ 1 l/m

The surface area of the samples must be adjusted accordingly if the oven volume differs from that in the example.

- › Oven drying time and oven temperature:
The stoving temperature and time to be used are calculated as the mean of the upper and lower limit of the processing range as stated in the instructions for use issued by the paint manufacturer.

The actual drying temperature and drying time must be logged and stated in the sample approval report. The samples for standard monitoring must be produced under the same temperature/stoving time conditions

Appendix 2 to the DaimlerChrysler Test Instructions PB VWL 709

- › On removal from the drying oven, the paints should be allowed to dry for 24 hours at room temperature (max. 23 °C). The surface of the paint must then be covered with aluminum foil and the samples packed into an airtight PE bag and sent to the analysis laboratory. Alternatively the samples can be stored after packing for up to 14 days at a maximum temperature of -18°C before being dispatched.

- › VOC/fog analysis in the laboratory (test instructions PB VWL 709)

The component supplier must submit a VOC/fog result from the Institut Fresenius for the first sample test report. This analysis may also have been commissioned by the paint manufacturer. This analysis must be no more than three years old and must relate to the current formulation. The shorter and cheaper analysis method in which only the total VOC or fog value is measured (see DB VWT 709) is sufficient for the standard monitoring required.

The analysis laboratory takes two 30 mm x 3 mm strips from the painted foil, weighs them and transfers them immediately to the thermodesorption tubes.

The basic weight of the aluminum foil must be deducted from the overall weighed amount to determine the actual weight of the paint. The analysis must therefore be provided with a blank sample of the aluminum foil used.

Further analysis is performed in accordance with the procedure set out in test instructions PB VWL 709.

Notes on standard painting:

Since the amount of solvent remaining in the paint film depends substantially on the drying conditions (particularly the temperature), compliance with the specified reference temperature is essential. Otherwise there is a risk that emissions in the vehicle interior may be higher.

Preparation of samples for wood paints

The film thickness of wood paints used in vehicle interiors is generally very large (approx. 800 µm).

This type of paint is therefore treated not as a "paint" (⇒ 50 µm film on aluminum) but as a plastics sample.

The wood paints are applied to aluminum foil and dried in accordance with standard production conditions.

Film thickness: 800 ± 50 µm,

Aluminum foil thickness: 30 µm (smooth surface).

Surface area: approx. DIN A4

The laboratory cuts a square piece from the painted foil measuring 10 mm x 3 mm (weighed amount: 30 mg ± 5 mg), weighs it **without aluminum foil** and transfers it immediately to the thermodesorption tubes for analysis.

Anlage 3

zur DaimlerChrysler-Prüfanweisung PE VWL 709

Chromatogramm-Reportausdruck im Excel-Format (Muster)

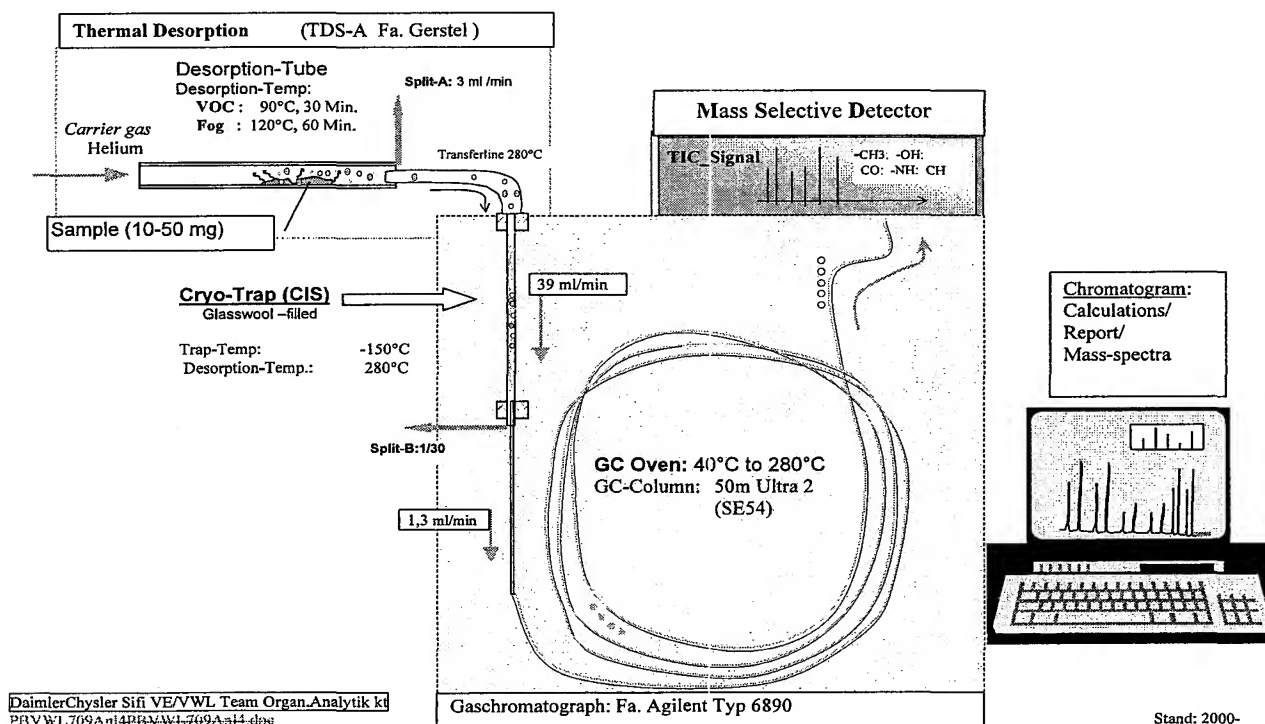
Thermodesorptionsanalyse					
File :	10991A.D	VWT-Nr. :			
Pfad:	CAHPCHEM\DATA\2000\5\	Externe Nr. :	1000_99/1001		
Operator:	Kt	Wareneingang:	10.12.2000		
Datum:	10.05.2000 00:00	Probenahme :	12.12.2000		
Methode:	VOC	Frod.Datum :			
Probe :	Musterbauteil, PUR-Folie DCX2000, Ch-Nr 444000555				
Info:	Musterlieferant, LxBxH 3x3,5x0,5mm 30,3 mg				
Rohr-Nr. :	4	DC-Sach-Nr	99900888		
VOC		Höchstwert	258	ppm	
		Zweitwert	241	ppm	
Retention Time(min.)	Substanzname	CAS-Nr.	Flächen(%)	ppm	Bewertung
3,82	2-Propanone (CAS) \$\$ Aceton	000067-64-1	0,5	1,4	
5,05	Acetic acid (CAS) \$\$ Essigsäure	000064-19-7	0,8	2	
19,22	1,3-Dioxolan-2-one (CAS) \$\$ Ethylene carbonate	000096-49-1	0,7	1,7	
21,97	? Massen 73 99 105	000000-00-0	0,4	0,9	
22,38	2-Ethyl-1-hexanol = "Isooctanol" = Isooctylalkohol	000104-76-7	0,4	1,0	
43,14	Öl (Isoalkane), Ret. 35 - 50 Min., Siedebereich ca. C14-C20		97,3	251	
Summe der identifizierten oder zugeordneten Substanzen			100	258	
Bemerkung:					

Stand: 2000-07-11

Datei: DDV\WV 709A\1200\WV 709A-12.doc

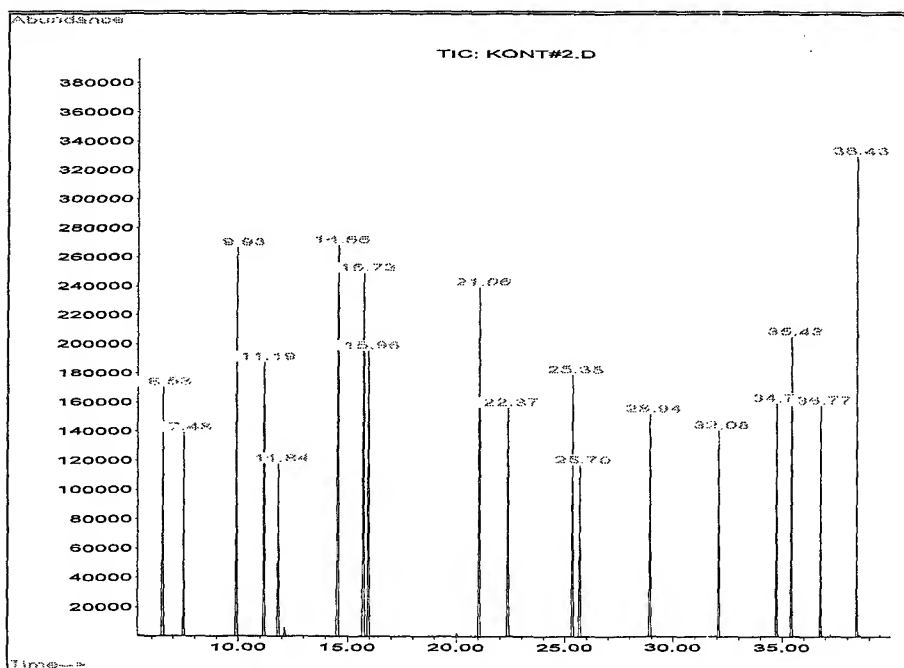
Anlage 4 zu DaimlerChrysler-Prüfanweisung PB VWL 709

Skizze Thermodesorptionsanalyse



Stand: 2000-

Anlage 5 zu DaimlerChrysler – Prüfanweisung PB VWL 709
Gaschromatogramm Kontrollmischung



Komponente	Ret-Zeit	Area	µg
Benzol	6.53	5124785	1,14
C7	7.48	3228221	0,91
Toluol	9.93	7632681	1,18
C8	11.19	5286993	0,96
n-Butylacetat	11.84	3416400	1,23
P/M-Xylol	14.56	9023794	1,18
O-Xylol	15.73	8508487	1,21
C9	15.96	6383404	1,00
C10	21.06	7521075	1,26
2-Ethylhexanol	22.37	4778433	1,12
C11	25.35	5023323	1,03
2,6-Dimethyl-phenol	25.70	3540155	0,64
C12	28.94	4120018	1,03
C13	32.08	3710219	1,04
C14	34.74	3411878	1,04
Dicyclohexylamin	35.43	4726648	1,23
C15	36.77	3224551	1,04
C16	38.43	6094852	1,95

2000-07-18
 PB VWL 709 Anlage 5 PB VWL 709 Anlage 5.doc

Appendix 6 to the DaimlerChrysler Test Instructions PB VWL 709

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

1 Limiting values/target values

The following requirements apply with immediate effect

1.1 Total emissions

VOC value	Target value: ≤ 100 ppm
Fog value	Target value: ≤ 250 ppm

F These requirements do not apply to the material-specific limiting values for VOC and fog as specified in the relevant DBLs.

1.2 Limiting values for individual substances for VOC and fog analysis

Corresponding to the categories in the latest MAC list published by the DFG ¹	
Carcinogenic	K1 K2 K3 A K3 B
Pregnancy	A B
Mutagenic	1 2 3 A 3 B
Allergic effect	H, S
Target: ≤ 8 ppm	

¹ From the latest edition: List of MAC and BAT values
Deutsche Forschungsgemeinschaft
Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe
Wiley-VCH Verlag GmbH D-69451 Weinheim, Germany